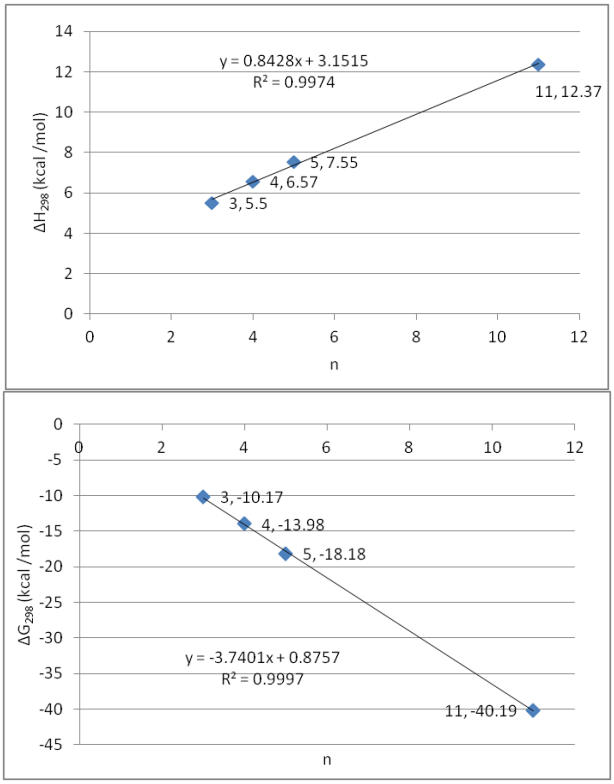
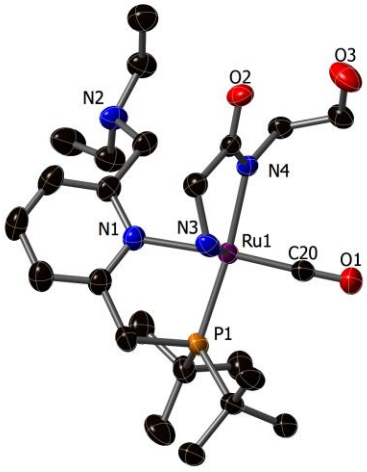
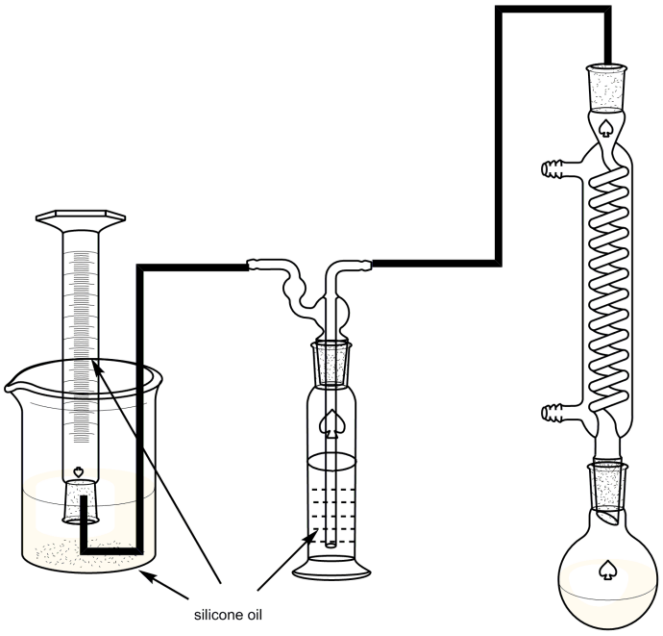


Supplementary Fig. 1 | Plot of ΔH_{298} (top) and ΔG_{298} (bottom) for Supplementary Equation 2 as a function of oligopeptide chain length (n). Also shown is the fitting of the data to a straight line.

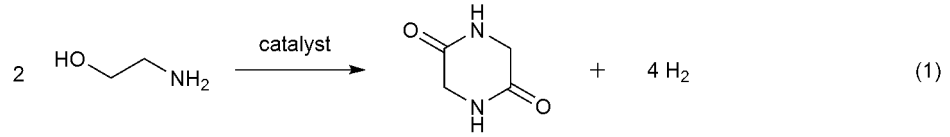


Supplementary Fig. 2 | X-ray structure of complex 8, showing ellipsoids at 50% level. Hydrogen atoms have been omitted for clarity. A CIF file is provided separately.



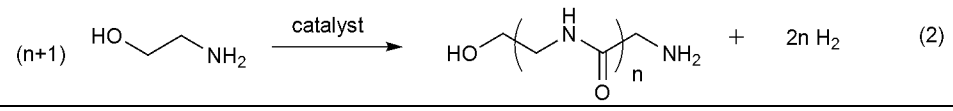
Supplementary Fig. 3 | Schematic drawing of the gas collection system.

Supplementary Table 1 | DFT calculations of 2-aminoethanol dehydrogenation to glycine anhydride



	Ee	E_0	H_{298}	G_{298}	ΔH_{298}	ΔG_{298}
reac	-419.97046	-419.77345	-419.76071	-419.82865	13.55	-6.08
prod	-419.91139	-419.7603	-419.73912	-419.83834		

Supplementary Table 2 | DFT calculations of 2-aminoethanol dehdrogenation to linear peptides



	Ee	E_0	H_{298}	G_{298}	ΔH_{298}	ΔG_{298}
reac (n = 3)	-839.94092	-839.54691	-839.52143	-839.6573	5.5	-10.17
prod (n = 3)	-839.8787	-839.55212	-839.51267	-839.67351		
reac (n = 4)	-1049.9261	-1049.4336	-1049.4018	-1049.5716	6.57	-13.98
prod (n = 4)	-1049.8443	-1049.4418	-1049.3913	-1049.5939		
reac (n = 5)	-1259.9114	-1259.3204	-1259.2821	-1259.486	7.55	-18.18
prod (n = 5)	-1259.8101	-1259.3317	-1259.2701	-1259.5149		
reac (n = 11)	-2519.8228	-2518.6407	-2518.5643	-2518.9719	12.37	-40.19
prod (n = 11)	-2519.6055	-2518.6718	-2518.5446	-2519.036		

Supplementary Table 3 | Solvent optimization for dehydrogenation of 2-aminoethanol catalyzed by complex 1.

Entry	Solvent (mL)	Conversion (%)	Product (yield %)
1	dioxane (4)	78	GA (48)+ LP
2	pyridine (4)	50	GA (trace)+ LP
3	diglyme (3), dioxane (1)	20	LP
4	toluene (3), dioxane (1)	75	GA (33)+ LP
5	toluene (3.5), dioxane (0.5)	62	GA (21)+ LP
6	DMF (3), dioxane (1)	0	none
7	*n*-BuCN (3), dioxane (1)	58	GA (10)+ LP
8	DMAc (3), dioxane (1)	0	none
9	NMM (3), dioxane (1)	34	GA (18)+ LP
10	NMM (0.5), dioxane (3.5)	61	GA (27)+ LP
11	NMM (1), dioxane (3)	67	GA (29)+ LP

Reaction conditions: 0.5 mol% catalyst **1**, 1.2 equiv of KO^{t}Bu to catalyst **1**, 1 mmol 2-aminoethanol and solvent were refluxed (the actual reaction temperature was 105 ^{0}C when using dioxane as the solvent, oil bath temperature 135 ^{0}C) under a flow of argon for 12 h. Conversion determined by NMR using 1,3,5-trimethylbenzene as an internal standard. Yields determined by NMR using pyridine as an internal standard. GA, glycine anhydride; LP, linear peptides; DMF, Dimethylformamide; DMAc, Dimethylacetamide; NMM, 4-methylmorpholine.

Supplementary Table 4 | Dehydrogenation of 2-aminoethanol catalyzed by 1 using a small amount of solvent or no solvent

Entry	Solvent[a] (mL)	Conversion (%)	Product[b] (yield)
1	none	48 (25)[c]	GA (trace)+ LP
2[d]	none	46	GA (trace)+ LP
3	DMSO (0.1)	61 (33)[c]	GA (trace)+ LP
4	DMSO (0.05)	59 (30)[c]	GA (trace)+ LP
5	DMSO (0.15)	63 (31)[c]	GA (trace)+ LP
6[e]	DMSO (0.1)	60 (31)[c]	GA (trace)+ LP
7[f]	DMSO (0.1)	67 (35)[c]	GA (trace)+ LP
8[g]	DMSO (0.1)	71 (39)[c]	GA (trace)+ LP
9[h]	dioxane (0.5)	57 (29)[c]	GA (trace)+ LP
10[h]	anisole (0.5)	62 (31)[c]	GA (trace)+ LP
11[h]	anisole (0.4) DMSO (0.1)	62 (32)[c]	GA (trace)+ LP
12[h]	DMSO (0.5)	42 (22)[c]	GA (trace)+ LP

Typical reaction conditions: 0.5 mol% catalyst **1**, 1.2 equiv (to catalyst **1**) KO^{t}Bu, 10 mmol 2-aminoethanol and solvent were heated (oil bath temperature 135 °C) under a flow of argon for 12 h. Conversions and yields were determined by NMR using pyridine as an internal standard. [a] DMSO, dimethyl sulfoxide. [b] GA, glycine anhydride; LP, linear peptides. [c] H_2 was collected, values in parentheses were yields of hydrogen based on the reaction of eq S3 (assuming 100% conversion to glycine anhydride). [d] Reflux under vacuum for 24 h, boiling point 110-124 °C, oil bath temperature 125 °C. [e] 0.5 mol% catalyst **8**, 1.2 mol% KO^{t}Bu were used. [f] Oil bath temperature 150 °C. [g] Oil bath temperature 170 °C. [h] 5 mmol of 2-aminoethanol was used.

Supplementary Table 5 | Repetitive reversal reactions catalyzed by 0.5 mol% complex 5

Cycle	Conversion of dehydrogenation[a]	Conversion of hydrogenation[a]
1	82	95 (94)
2	73 (77)	80 (73)
3	61 (76)	70 (51)

0.5 mol% complex **5** was used. [a]Based on the amount of 2-aminoethanol in the system. The number in parenthesis is based on the product of the former step.

Supplementary Note 1

Complex **5** may be capable of MLC by both ligand amine-amide and aromatization-dearomatization modes. That is, in the presence of two equivalents of base, not only the PNNH arm is deprotonated, but also the NH^{t}Bu group of complex **5** can be deprotonated. The two MLC modes can both promote dehydrogenation and hydrogenation reactions. If the two modes work together in one catalytic system, the catalytic activity is expected to be higher than that with the normal PNN ruthenium pincer complexes (such as complexes **1**, **3** and **4**), since each step in the catalytic cycle can follow the lowest energy path of the two modes. The anionic, double deprotonated, dearomatized enamido Ru complex generated from **5** was reported by us.[8] For examples of the higher catalytic activity in dehydrogenation and hydrogenation using complex **5**, see also reference 8.

Supplementary Note 2

Attempts of using no solvent or a small amount of solvent resulted in lower efficiency of the dehydrogenative coupling reaction (Supplementary Table 4). When applying 0.5 mol% catalyst **1** and 0.6 mol% KO^{t}Bu in neat 2-aminoethanol at 135 °C for 12 h, 48% conversion was achieved. However, just 27% yield of hydrogen gas was collected, together with 2-amino-*N*-(2-hydroxyethyl)acetamide (AA) and some other short-chain linear peptides (n = 2, 3) as the major products (entry 1). Refluxing 2-aminoethanol under mild vacuum (~80 mm Hg) at 110-124 °C resulted in similar conversion (entry 2). DMSO was found to be a helpful additive for the reaction (entries 3-8). A small amount of DMSO (0.1 mL DMSO per 10 mmol 2-aminoethanol) improved the yield of H_2 from 27% to 35% at 135 °C (entry 1 *vs* 3). Catalyst **5** gave similar results as compared to catalyst **1** under the same conditions (*c.f.* entries 3 and 6). Higher temperature slightly increased the outcome of the reaction (entries 7, 8) and 42% yield of H_2 was obtained when heating the reaction to 170 °C for 12 h (entry 8). 0.5 mL of dioxane, anisole and mixture of anisole /DMSO (4:1 in volume) had similar effects on the reaction and approximate 30% yield of H_2 was produced (entries 9-11). When 0.5 mL DMSO was used solely as the solvent, H_2 was obtained in just 24% yield (entry 12).

Supplementary Note 3

Useful Information of the intermediates with complex **5** as pre-catalyst was not obtained. However, an anionic, double deprotonated, dearomatized enamido Ru complex, which was generated from **5** upon treatment with 2.5 equiv of base, was obtained by us as reported in reference 8. In addition, because catalyst **1** exhibits similar catalytic activity as catalyst **5** (though not as good), the study of it does provide useful mechanistic insight, relevant, at least in part, to both systems.

Supplementary Discussion

The DFT results indicate that both ΔH_{298} and ΔG_{298} of Supplementary Equation 2 show linear dependence with the length (n) of the linear peptides produced. With a larger n, ΔH_{298} increases while ΔG_{298} decreases. From the results in Supplementary Tables 1 and 2, one notes that the formation of linear oligopeptides is thermodynamically more favorable than formation of diketopiperazine (glycine anhydride).

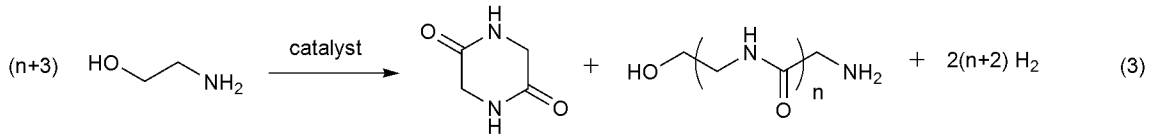
Supplementary Methods

General Information. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were purified according to standard procedures under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glove box over 4Å molecular sieves. Most of the chemicals used in the catalytic reactions were purified according to standard procedures (vaccum distillation).[1] Complexes **1-4** were prepared by our reported methods.[2-5] $RuHCl(PPh_3)_3(CO)$[6], 2-($ClCH_2$-)-6-($^tBu_2P(BH_3)CH_2$-)pyridine[7] were prepared according to literature procedures. The ligand PNN-H ((2-(($^tBu_2$)PCH_2-)-6-((^{t}Bu)$NHCH_2$-)pyridine) and complex **5** were reported by us very recently.[8]

^1H, ^{13}C and ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. Measurements were done at various temperatures, as noted for each experiment. ^1H NMR chemical shifts are referenced to the residual hydrogen signals of the deuterated solvent, and the ^{13}C NMR chemical shifts are referenced to the ^{13}C signals of the deuterated solvent. ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Abbreviations used in the description of NMR data are as follows: Ph, phenyl; Py, pyridyl; br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual; bm, broad multiplet; bs, broad singlet. IR spectra were recorded on a Nicolet FT-

IR spectrophotometer. Mass spectra were recorded on MicromassPlatform LCZ 4000. X-ray data were collected on Nonius KappaCCD diffractometer, MoKα (λ=0.71073Å), equipped with graphite monochromator and Miracol collimator.

General procedure for the dehydrogenation of 2-aminoethanol. In a glove box, a 25 mL Schlenk flask was charged with a stirring bar, catalyst (0.005 mmol), KO^{t}Bu (0.006-0.012 mmol), 2-aminoethanol (1 mmol) and dioxane (4 mL) under an atmosphere of nitrogen. The flask was taken out of the glove box, equipped with a condenser and the solution was refluxed with stirring in an open system under a flow of argon for 12 h. After cooling to room temperature, 1 mmol of 1,3,5-trimethylbenzene was added to the crude reaction mixture as an internal standard. Then 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion of 2-aminoethanol by ^{1}H NMR spectroscopy. To the rest of the solution was added 10-15 mL hexane and the mixture was cooled down to 0 °C. The formed precipitate was collected by simple filtration and washed with 10 mL of hexane and dried under vacuum. 1 mmol pyridine was then added to the dry solid as an internal standard and the mixture was analyzed by ^{1}H NMR spectroscopy to determine the yield of glycine anhydride (GA), using D_2O as the solvent.



(3)

MS (ESI) of products obtained under conditions of Table 1, entry 13: 119.02 (linear peptide (n = 1) + H), 141.03 (linear peptide (n = 1) + Na), 198.05 (linear peptide (n = 2) + Na), 233.06 (GA + linear peptide (n = 1) + H), 255.13 (GA + linear peptide (n = 1) + Na or linear peptide (n = 3) + Na), 312.21 (linear peptide (n = 4) + Na), 369.15 (linear peptide (n = 5) + Na), 430.34 (linear peptide (n = 6) + 4H + Na), 453.17 (linear peptide (n = 6) + 4H + 2Na).

MS (CI): 112.93 (GA - H), 116.99 (linear peptide (n = 1) - H), 174.01 (linear peptide (n = 2) - H), 231.03 (GA + linear peptide (n = 1) - H), 288.30 (linear peptide (n = 4) - H), 402.25 (linear peptide (n = 6) - H).

General procedure for the hydrogenation of glycine anhydride. In a glove box, a 100 mL Fischer-Porter tube or a 20 mL Parr apparatus was charged with catalyst (0.005 mmol), KO^{t}Bu (0.006-0.012 mmol), glycine anhydride (0.5-1.0 mmol) and dioxane or THF (2 or 4 mL) under an atmosphere of purified nitrogen. The pressure equipment was taken out of the glove box and subjected to three successive cycles of pressurization/venting with H_2 (3 atm), then pressurized with H_2 (10-50 bar) and closed. The pressure equipment was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 24-48 h. After cooling to room temperature, excess H_2 was carefully vented off. The unreacted glycine anhydride was filtered off washed with 10 mL of hexane and dried under vacuum. To the dry solid 1 mmol of pyridine was added as an internal standard, and the mixture was dissolved in D_2O for determination of the amount of glycine anhydride by ^{1}H NMR spectroscopy. The filtrate was collected and evaporated under vacuum to give a mixture. To the mixture was added 1 mmol of pyridine as an internal standard, dissolved in D_2O and analyzed by ^{1}H NMR spectroscopy to determine the yield of 2-aminoethanol and the amount of glycine anhydride in solution. The total amount and the relative conversion of glycine anhydride were obtained in this way (the reason for this procedure is inaccurate determination of 2-aminoethanol in the presence of a large amount of glycine anhydride).

General procedure for gas collection. In a glove box, a 25 mL Schlenk flask was charged with a stirring bar, catalyst (0.005 mmol), KO^{t}Bu (0.006-0.012 mmol), 2-aminoethanol (1 mmol) and dioxane (4 mL) under an atmosphere of nitrogen. The flask was taken out of the glove box, equipped with a reflux condenser and connected to a gas collection system under a flow of argon. The whole open system was flushed with argon and then connected to an inverted graduated cylinder filled with silicon oil (see Supplementary Fig. 3). The solution was refluxed with stirring and after 9 hrs no more gas bubbles were observed. After 12 h the volume of the generated gas was recorded as V1. To quantify the effect of warming on the gas volume, the condenser was disconnected from the gas collection system and opened in the air. After the flask was cooled to room temperature, the condenser was connected to the gas collection system again. The solvent was refluxed for another 0.5 h until no gas bubbles (as a result of

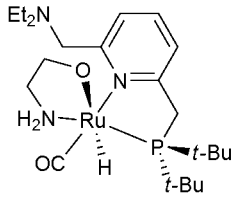
argon expansion) were observed, and the increased volume of gas in the flask when heating was recorded as V2. The volume of H_2 produced was V1-V2.

Procedure for 20 mmol scale dehydrogenation reaction. In a glove box, a 250 mL Schlenk flask was charged with a stirring bar, catalyst **5** (0.1 mmol), KO^{t}Bu (0.24 mmol), 2-aminoethanol (20 mmol) and dioxane (80 mL) under an atmosphere of nitrogen. The flask was taken out of the glove box, equipped with a reflux condenser and connected to a gas collection system under a flow of argon. The whole open system was flushed with argon and then connected to an inverted graduated cylinder filled with silicon oil (see Supplementary Fig. 3). The solution was refluxed with stirring for 12 h. After cooling to room temperature, 4 mmol of 1,3,5-trimethylbenzene was added to the crude reaction mixture as an internal standard. Then 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion of 2-aminoethanol by ^{1}H NMR spectroscopy. To the rest of the solution was added 100 mL hexane and the mixture was cooled down to 0 °C. The formed precipitate was collected by simple filtration and washed with 3×30 mL of hexane and dried under vacuum. 10 mmol of pyridine was then added to the dry solid as an internal standard and the mixture was dissolved with 10 mL H_2O. Then 0.05 mL of the solution was added with D_2O to determine the yield of glycine anhydride (GA) by ^{1}H NMR spectroscopy.

Procedure for 5 mmol scale hydrogenation reaction. The general procedure for the hydrogenation of glycine anhydride was followed with Complex **5** (1 mol%), KO^{t}Bu (2.4 mol%), GA (5 mmol), and dioxane (5 mL) under 70 bar of H_2 for 12 h.

Formation of 6. In a glove box, a vial was charged with 1.8 mg (0.03 mmol) or 12.2 mg (0.2 mmol) of 2-aminoethanol. A solution of 9 mg (0.02 mmol) of complex **2** ((^{t}BuPNN)Ru(H)(CO)) in 0.5-0.6 mL C_6D_6 or toluene-d_8 was added. After shaking for 2 min, the color changed from brown to dark red and the solution was transferred to a NMR tube and analyzed by NMR. The sample dissolved in toluene-d_8 was analyzed at –30 °C. Samples dissolved in C_6D_6 were analyzed at room temperature. Complex **6** was

produced in nearly quantitative yield in 15 min, which was observed by ^{1}H (Fig. 4a) and $^{31}P\{^{1}H\}$ (Fig. 4b,c) NMR spectroscopy.



6

$^{31}P\{^{1}H\}$ NMR (162MHz, C_6D_6, 20 °C): 105.6 (s).

$^{31}P\{^{1}H\}$ NMR (162MHz, toluene-d_8, -30 °C): 106.3 (s).

^{1}H NMR (400MHz, C_6D_6, 20 °C): 6. 99-6.92 (m, 2H, Py-H_{meta} and Py-H_{para}), 6.76 (d, J_{HH} = 7.0 Hz, 1H, Py-H_{meta}), 5.10 (dd, J_{HH} = 14.3 Hz, J_{PH} = 8.7Hz, 1H, -CH*H*P), 4.58 (br, 1H, -N*H*H), 4.10 (d, J_{HH} = 13.0 Hz, 1H, -CH*H*NEt_2), 3.95-3.90 (m, 1H, -CH*H*O), 3.68-3.63 (m, 1H, -CH*H*O), 3.59 (d, J_{HH} = 12.9 Hz, 1H, -CH*H*NEt_2), 3.07 (t, J_{HH} = 13.3 Hz, J_{PH} = 13.3Hz, 1H, -CH*H*P), 2.83 (br, 1H, -N*H*H), 2.51-2.40 (m, 3H, -N(CH_2Me)$_2$ and -C*H*HNH_2), 2.29-2.19 (m, 2H N(CH_2Me)$_2$), 2.09 (br, 1H, -C*H*HNH_2), 1.60 (d, J_{PH} = 12.8 Hz, 9H, P-C(CH_3)$_3$), 1.01 (d, J_{PH} = 12.0 Hz, 9H, P-C(CH_3)$_3$), 0.86 (t, J_{HH} = 7.1 Hz, 6H, N(CH_2CH_3)$_2$), -14.22 (d, J_{PH} = 18.9 Hz, 1H, Ru-*H*).

^{1}H NMR (400MHz, toluene-d_8, -30 °C): 6. 97-6.95 (m, *overlapped with peak of toluene*, 1H, Py-H_{para}), 6.76 (d, J_{HH} = 7.0 Hz, 1H, Py-H_{meta}), 6.70 (d, J_{HH} = 7.5Hz, 1H, Py-H_{meta}), 5.27 (br, 1H, -N*H*H), 4.89 (dd, J_{HH} = 14.7 Hz, J_{PH} = 7.7Hz, 1H, -CH*H*P), 4.12 (d, J_{HH} = 12.3 Hz, 1H, -CH*H*NEt_2), 3.82-3.78 (m, 1H, -CH*H*O), 3.54-3.51 (m, 1H, -CH*H*O), 3.20 (d, J_{HH} = 12.2 Hz, 1H, -CH*H*NEt_2), 3.02 (dd, J_{HH} = 14.7 Hz, J_{PH} = 13.1Hz, 1H, -CH*H*P), 2.62 (br, 1H, -N*H*H), 2.43-2.34 (m, 2H, N(CH_2Me)$_2$), 2.30 (br, 1H, -C*H*HNH_2), 2.04-1.99 (m, *overlapped with the peak of toluene*, 3H, N(CH_2Me)$_2$ and -C*H*HNH_2), 1.53 (d, J_{PH} = 12.7 Hz, 9H, P-C(CH_3)$_3$), 0.92 (d, J_{PH} = 11.8 Hz, 9H, P-C(CH_3)$_3$), 0.79 (t, J_{HH} = 6.9 Hz, 6H, N(CH_2CH_3)$_2$), -14.11 (d, J_{PH} = 18.6 Hz, 1H, Ru-*H*).

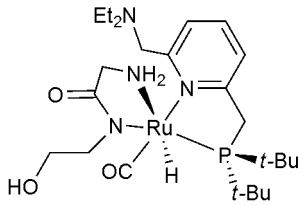
$^{13}C\{^{1}H\}$ NMR (100MHz, toluene-d_8, -30 °C): 208.03 (d, J_{PC} = 15.4 Hz, Ru-*C*O), 164.86 (d, J_{PC} = 2.3 Hz, C_{Py}-CH_2-P), 159.70 (s, C_{Py}-CH_2-N), 135.76 (s, C_{Py}-H_{para}), 123.04 (s, *C*H-C(N)-CH_2-N), 122.80 (d, J_{PC} = 6.6 Hz, *C*H-C(N)-CH_2-P), 69.16 (d, J_{PC} = 4.2 Hz, O-*C*H_2-CH_2), 61.36 (s, Py-*C*H_2-N), 47.35 (s, NH_2-*C*H_2-CH_2), 45.86 (s, N(*C*$H_2CH_3)_2$), 36.14 (d, J_{PC} = 16.8 Hz, P-*C*$(CH_3)_3$), 35.01 (d, J_{PC} = 20.1 Hz, P-*C*$(CH_3)_3$), 34.82 (d, J_{PC} = 12.2 Hz, Py-*C*H_2-P), 30.37 (d, J_{PC} = 4.1 Hz, P-C(*C*H3)3), 29.31 (d, J_{PC} = 2.4 Hz, P-C(*C*H3)3), 10.89 (s, N(CH_2*C*$H_3)_2$).

^{1}H and ^{13}C signal assignments were confirmed by $^{1}H\{^{31}P\}$, ^{1}H COSY, ^{13}C DEPTQ, ^{13}C-^{1}H HSQC and NOESY.

IR (benzene, plate): *v* C-O 1907 cm^{-1}.

Because complex **6** is not stable, HRMS was not obtained.

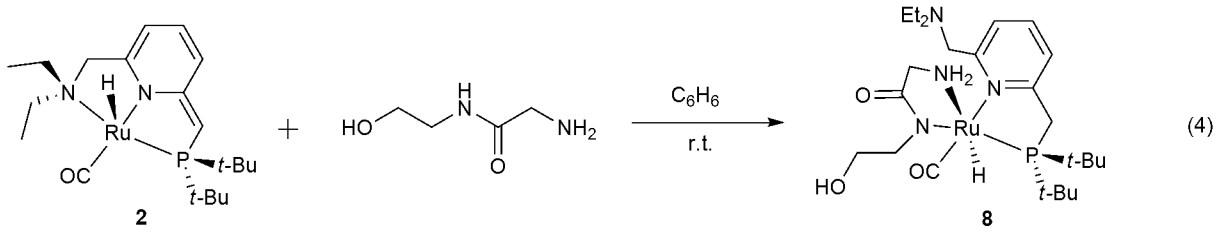
Formation of 8.



8

In a glove box, a 5 mL vial was charged with 1.8 mg (0.03 mmol) of 2-aminoethanol and a solution of 9 mg (0.02 mmol) of complex **2** ((^{t}BuPNN)Ru(H)(CO)) in 0.5-0.6 mL C_6H_6. After shaking for 2 min, the color changed from brown to dark red. Then the open 5 mL vial was placed in a 20 mL vial which contained ~5 mL pentane. The 20 mL vial was closed tightly with a cap to let slow diffusion of pentane into the benzene solution in the 5 mL vial. After 2 weeks, crystals suitable for X-ray analysis were obtained. The procedure was repeated and the crystals were carefully collected, washed with benzene, dried (2.4 – 4.3 mg pure complex was obtained every time) and dissolved in acetone-d_6 or THF-d_8 for NMR study.

Independent preparation of complex 8.



(4)

In a glove box, a 5 mL vial was charged with a stirring bar, 2.8 mg (0.024 mmol) of 2-amino-*N*-(2-hydroxyethyl)acetamide and a solution of 9 mg (0.02 mmol) of complex **2** ((^{t}BuPNN)Ru(H)(CO)) in 0.5-0.6 mL C_6H_6. After stirring for 1-2 days, the solution was clear and the insoluble solid disappeared. The open 5 mL vial was placed in a 20 mL vial which contained ~5 mL pentane. The 20 mL vial was closed tightly with a cap to let slow diffusion of pentane into the benzene solution in the 5 mL vial. After 2 weeks, crystals suitable for X-ray analysis were obtained.

$^{31}P\{^1H\}$ NMR (162MHz, acetone-d_6, 20 °C): 100.7 (s)

^1H NMR (400MHz, acetone-d_6, 20 °C): 7.80 (t, J_{HH} = 7.6 Hz, 1H, Py-H_{para}), 7.75 (d, J_{HH} = 7.6 Hz, 1H, Py-H_{meta}, the one close to -NEt_2), 7.47 (d, J_{HH} = 7.6 Hz, 1H, Py-H_{meta}, the one close to -P(^{t}Bu)$_2$), 4.28-4.23 (m, 1H, -CH*H*CH_2OH), 4.04 (d, J_{HH} = 16.7 Hz, 1H, -CH*H*NEt_2), 3.92 (td, J_{HH} = 10.1, 1.9 Hz, 1H, -CH*H*OH), 3.87 (d, J_{HH} = 16.7 Hz, 1H, -CH*H*NEt_2), 3.80-3.68 (m, 3H, -CH*H*OH and –CH_2P), 3.51-3.47 (m, 1H, -CH*H*CH_2OH), 3.02 (dd, J_{HH} = 14.7, 5.8 Hz, 1H, -CH*H*NH_2), 2.65-2.61 (bm, 1H, -N*H*H), 2.58-2.49 (m, 2H, N(CH_2Me)$_2$), 2.47-2.39 (m, 2H, N(CH_2Me)$_2$), 1.99-1.91 (m, -C*H*HNH_2), 1.41 (d, J_{PH} = 12.7 Hz, 9H, P-C(CH_3)$_3$), 1.08 (d, J_{PH} = 12.7 Hz, 9H, P-C(CH_3)$_3$), 1.02 (t, J_{HH} = 7.1 Hz, 6H, N(CH_2CH_3)$_2$), -13.49 (d, J_{PH} = 23.4 Hz, 1H, Ru-*H*). The proton of –OH and one proton of –NH_2 were not observed.

$^{13}C\{^1H\}$ NMR (100MHz, acetone-d_6, 20 °C): 208.84 (d, J_{PC} = 15.6 Hz, Ru-*C*O), 178.75 (d, J_{PC} = 1.4 Hz, *C*=O),166.37 (s, C_{Py}-CH_2-N), 162.64 (d, J_{PC} = 5.6 Hz, C_{Py}-CH_2-P), 138.44 (s, C_{Py}-H_{para}), 122.87(d, J_{PC} = 8.1 Hz, *C*H-C(N)-CH_2-P), 122.07(s, *C*H-C(N)-CH_2-N), 66.20 (s, *C*H_2-OH), 61.78 (s, *C*H_2-NEt_2), 58.44 (s, *C*H_2-CH_2-OH), 48.76 (s, *C*H_2-

NH_2), 48.01 (s, N(*C*$H_2CH_3)_2$), 36.05 (d, J_{PC} = 23.4 Hz, P-(*C*$(CH_3)_3)_2$), 35.77 (d, J_{PC} = 17.6 Hz, *C*H_2-P), 29.67 (s, P-C(*C*H3)3), 28.08 (s, P-C(*C*H3)3), 12.43 (s, N(CH_2*C*$H_3)_2$).

$^{31}P\{^1H\}$ NMR (162MHz, THF-d_8, 20 °C): 101.2 (s)

^{1}H NMR (400MHz, THF-d_8, 20 °C): 7.71 (d, J_{HH} = 7.5 Hz, 1H, Py-H_{meta}, the one close to -NEt_2), 7.65 (t, J_{HH} = 7.5 Hz, 1H, Py-H_{para}), 7.33 (d, J_{HH} = 7.5 Hz, 1H, Py-H_{meta}, the one close to -P(^{t}Bu)$_2$), 5.41 (dd, J_{HH} = 2.3, 6.0 Hz, 1H, -O*H*), 4.27-4.21 (m, 1H, -CH*H*CH_2OH), 4.06 (d, J_{HH} = 16.9 Hz, 1H, -CH*H*NEt_2), 3.94-3.80 (m, 4H, -CH*H*OH, –CH*H*P, -N*H*H and -CH*H*NEt_2), 3.30-3.65 (m, 1H, -CH*H*OH), 3.64-3.57 (m, 1H, –CH*H*P, *overlapped with peak of THF*), 3.46-3.42 (m, -CH*H*CH_2OH), 2.80 (dd, J_{HH} = 14.8, 5.1 Hz, 1H, -CH*H*NH_2), 2.72-2.68 (bm, 1H, -N*H*H), 2.56-2.47 (m, 2H, N(C*H*$_2$Me)$_2$), 2.47-2.38 (m, 2H, N(C*H*$_2$Me)$_2$), 1.77-1.70 (m, 1 H, -C*H*HNH_2, *overlapped with peak of THF*), 1.37 (d, J_{PH} = 12.6 Hz, 9H, P-C(C*H*$_3)_3$), 1.03 (d, J_{PH} = 12.6 Hz, 9H, P-C(C*H*$_3)_3$), 1.03 (t, J_{HH} = 6.9 Hz, 6H, N(CH_2C*H*$_3)_2$), -13.45 (d, J_{PH} = 23.3 Hz, 1H, Ru-*H*).

$^{13}C\{^1H\}$ NMR (100MHz, THF-d_6, 20 °C): 208.50 (d, J_{PC} = 15.1 Hz, Ru-*C*O), 178.60 (s, *C*=O),167.28 (s, C_{Py}-CH_2-N), 162.60 (d, J_{PC} = 5.6 Hz, C_{Py}-CH_2-P), 137.82 (s, C_{Py}-H_{para}), 122.35 (d, J_{PC} = 7.9 Hz, *C*H-C(N)-CH_2-P), 122.18 (s, *C*H-C(N)-CH_2-N), 66.61 (s, *C*H_2-OH), 62.13 (s, *C*H_2-NEt_2), 58.71 (s, *C*H_2-CH_2-OH), 49.52 (s, *C*H_2-NH_2), 48.28 (s, N(*C*$H_2CH_3)_2$), 36.25 (d, J_{PC} = 22.6 Hz, P-*C*$(CH_3)_3$), 35.93 (d, J_{PC} = 16.1 Hz, P-*C*$(CH_3)_3$), 34.94 (d, J_{PC} = 14.6 Hz, *C*H_2-P), 29.78 (d, J_{PC} = 3.8 Hz, P-C(*C*H3)3), 28.34 (d, J_{PC} = 4.0 Hz, P-C(*C*H3)3), 12.56 (s, N(CH_2*C*$H_3)_2$).
^{1}H and ^{13}C signal assignments were confirmed by $^1H\{^{31}P\}$, ^{1}H COSY, ^{13}C DEPTQ, ^{13}C-^{1}H HSQC.

IR (film): 1947, 1896, 1568 cm^{-1}

HRMS calcd for $C_{20}H_{36}N_2OPRu$ $[M – (HOCH_2CH_2NCOCH_2NH_2)]^+$: 453.1609, found: 453.1575.

Synthesis of 2-amino-*N*-(2-hydroxyethyl)acetamide. This compound has been reported[9]. Herein we report a new procedure to produce it in one step from glycine anhydride.

In a glove box, a 20 mL Parr reactor was charged with complex **1** (0.01 mmol), KO^{t}Bu (0.012 mmol), glycine anhydride (0.5 mmol) and dioxane (4 mL) under an atmosphere of purified nitrogen. The Parr reactor was taken out of the glove box and subjected to three successive cycles of pressurization/venting with H_2 (3 atm), then pressurized with H_2 (50 bar) and closed. The Parr reactor was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 48 h. After cooling to room temperature, excess H_2 was vented off carefully. The solution was collected and the solvent was evaporated under vacuum to give a solid. The solid was purified by recrystallization (methanol-ether) and 36 mg (61%) pure 2-amino-*N*-(2-hydroxyethyl)acetamide was obtained as a white solid.

^{1}H NMR (D_2O): 3.48 (t, J = 5.5 Hz, 2H), 3.16 (t, J = 5.5 Hz, 2H), 3.10 (s, 2H). ^{13}C{^{1}H} NMR (D_2O): 175.46, 59.85, 43.62, 41.17. HRMS calcd for $C_4H_{10}N_2O_2Na$ $[M + Na]^+$: 141.0640, found: 141.0635.

Crystal data of complex **8**: $4C_{24}H_{45}N_4O_3PRu + C_5H_{12}$, light yellow chunk, 0.20 x 0.20 x 0.20 mm^3, Tetragonal *I4$_1$/a*, a=16.7084(1)Å, c=43.4667(4)Å, $2\theta_{max}$=27.47°, T=120(2)K, V=12134.6(2)Å^3, Z=4, Fw=2350.87, Dc=1.287 Mg·m^{-3}, μ=0.599 mm^{-1}. Data collection of 116835 reflections collected, 7073 independent reflections (R-int =0.073). The data were processed with DENZO[10]. $-21 \le h \le 21$, $-21 \le k \le 21$, $-56 \le l \le 56$. Structure solved with DIRDIF[11]. Full matrix least-squares refinement based on F^2 with SHELXL-97[12] on 334 parameters with 3 restraints gave final R_1= 0.0458 (based on F^2) for data with $I>2\sigma(I)$ and, R_1= 0.0629 on 6948 reflections, goodness-of-fit on F^2 = 1.038, largest electron density peak 1.549 e·Å^{-3}. Largest hole –0.683 e·Å^{-3}. All hydrogens were calculated except the hydride and the N3 hydrogens that were located in the density map. Crystallographic data of complex **8** has been deposited at the Cambridge Crystallographic Data Centre (CCDC-1017722).

Procedures for dehydrogenation of 2-aminoethanol catalyzed by complex 8. The general procedure for the dehydrogenation of 2-aminoethanol was followed with Complex **8** (0.5 mol%), KO^{t}Bu (1.2 mol%), 2-aminoethanol (1 mmol) and dioxane (4 mL). Results: 81% conversion of AE, 33% yield of GA.

Computational Methods. All computations used GAUSSIAN09 REVISION C.01[13]. Geometries were optimized with Adamo and Barone's hybrid version (PBE0)[14] of the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE)[15,16]. The SVP double-ζ quality basis set[17,18] was used.

Procedure for the repetitive reversal reactions: a) Using 0.5 mol% complex **5** (Supplementary Table 5): In a glove box, a 25 mL Schlenk flask was charged with a stirring bar, catalyst **5** (0.005 mmol), KO^{t}Bu (0.012 mmol), 2-aminoethanol (1 mmol) and dioxane (4.5 mL) under an atmosphere of nitrogen. The flask was taken out of the glove box, equipped with a condenser and the solution was refluxed with stirring in an open system under a flow of argon for 8 h. After cooling to room temperature, the flask was sealed under a flow of argon and taken into a glove box. 1 mmol of 1,3,5-trimethylbenzene was added to the crude reaction mixture as an internal standard. Then 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion of 2-aminoethanol by ^{1}H NMR spectroscopy. All of the rest of the solution and precipitate were transferred to a 20 mL Parr apparatus. A catalytic amount of KO^{t}Bu (0.012 mmol) was also added to protect the catalyst from trace amount of water, which may be taken into the system during the course of transfer. The Parr apparatus was taken out of the glove box and subjected to three successive cycles of pressurization/venting with H_2 (3 atm), then pressurized with H_2 (60 bar) and closed. The Parr apparatus was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 10 h. After cooling to room temperature, excess H_2 was carefully vented off. The Parr apparatus was taken into the glove box again and 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion by ^{1}H NMR spectroscopy. The reaction mixture was then transferred to a 25 mL Schlenk flask together with 0.012 mmol KO^{t}Bu. The flask was taken out of the glove box equipped

with a condenser and the solution was refluxed with stirring in an open system under a flow of argon for 11 h. The last hydrogenation and dehydrogenation steps were repeated, the reaction time were 10 h and 11 h, respectively. b) Using 1 mol% complex **5**: In a glove box, a 25 mL Schlenk flask was charged with a stirring bar, catalyst **5** (0.01 mmol), KO^{t}Bu (0.024 mmol), 2-aminoethanol (1 mmol) and dioxane (4.5 mL) under an atmosphere of nitrogen. The flask was taken out of the glove box, equipped with a condenser and the solution was refluxed with stirring in an open system under a flow of argon for 5 h. After cooling to room temperature, the flask was sealed under a flow of argon and taken into a glove box. 1 mmol of 1,3,5-trimethylbenzene was added to the crude reaction mixture as an internal standard. Then 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion of 2-aminoethanol by ^{1}H NMR spectroscopy. All of the rest solution and precipitate were transferred to a 20 mL Parr apparatus. A catalytic amount of KO^{t}Bu (0.024 mmol) was also added to protect the catalyst from trace amount of water, which may be taken into the system during the transfer. The Parr apparatus was taken out of the glove box and subjected to three successive cycles of pressurization/venting with H_2 (3 atm), then pressurized with H_2 (60 bar) and closed. The Parr apparatus was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 5 h. After cooling to room temperature, excess H_2 was carefully vented off. The Parr apparatus was taken into the glove box again and 0.05 mL of the solution was dissolved in $CDCl_3$ for determination of the conversion by ^{1}H NMR spectroscopy. The reaction mixture was then transferred to a 25 mL Schlenk flask together with 0.024 mmol KO^{t}Bu. The flask was taken out of the glove box equipped with a condenser and the solution was refluxed with stirring in an open system under a flow of argon for 11 h. The last hydrogenation and dehydrogenation steps were repeated, the reaction time were 10 h and 11 h, respectively. Results are given in the manuscript, Table 3.

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